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Changes in the ionic composition of a saline lake, Mar Chiquita, Province of Córdoba, Argentina

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Abstract. Mar Chiquita is the largest water-body in Argentina according to area. This ranges from 2,000 km^2 in dry periods to 5,000 km^2 in humid ones. Its very high salinity ranged this century from 200 to 300 g/L, but an increase in the average rainfall in the basin since 1973 has led to a rise in lake level and the dilution of its waters to 78 g/L in 1978 and about 30 g/L in the late 1980s. Ionic strength decreased from 6.61 in 1970 to 0.541 in 1986. The composition of the water also changed, with increases in the proportions of sulphate, calcium and magnesium concentrations. The most important processes taking place in solution are calcite and gypsum equilibrium, formation of clay minerals, and sulphate reduction in the interstitial waters of the bottom sediments. The thermodynamic state of the solutions for different years has been obtained. Results show that the solution shifted from gypsum oversaturation in 1970 to gypsum equilibrium in 1978, and to gypsum undersaturation since 1982. A geochemical simulation of the composition of the solution from its origin from mean tributary composition, following a modified Hardie-Eugster model, has been developed using PHRQPITZ. The results agree with empirical observations.

Key words: Argentina, ionic composition, Mar Chiquita, saline

Introduction

The evolution of non-marine brines has been discussed by many since the papers of Garrels and Mckenzie (1967) and Hardie and Eugster (1970). The Hardie-Eugster model has been applied to Lake Chad (Eugster and Hardie, 1978), Lake Magadi (Eugster, 1970; Jones *et al.*, 1977), and elsewhere. However, it has not thus far been applied to salt lakes in Argentina. The present paper does so, and on the basis of the observed changes in the composition of Mar Chiquita Lake, the Hardie-Eugster model appears to be a useful tool in understanding changes in the composition of the waters of this lake.

Mar Chiquita lies in the north-east of the Province of Córdoba, República Argentina, between 30°20′ and 31°00′ S lat. and 62°10′ and 63°10′ W long., in the geomorphological area known as Llanura Chaco Pampeana (Fig. 1). The lake is the largest water-body in the country according to area and is well known because of its high salinity. This high salinity and the smell of its muds, believed to have therapeutic properties, have led to the development of an important lakeside resort in the past decades. To the south and east of

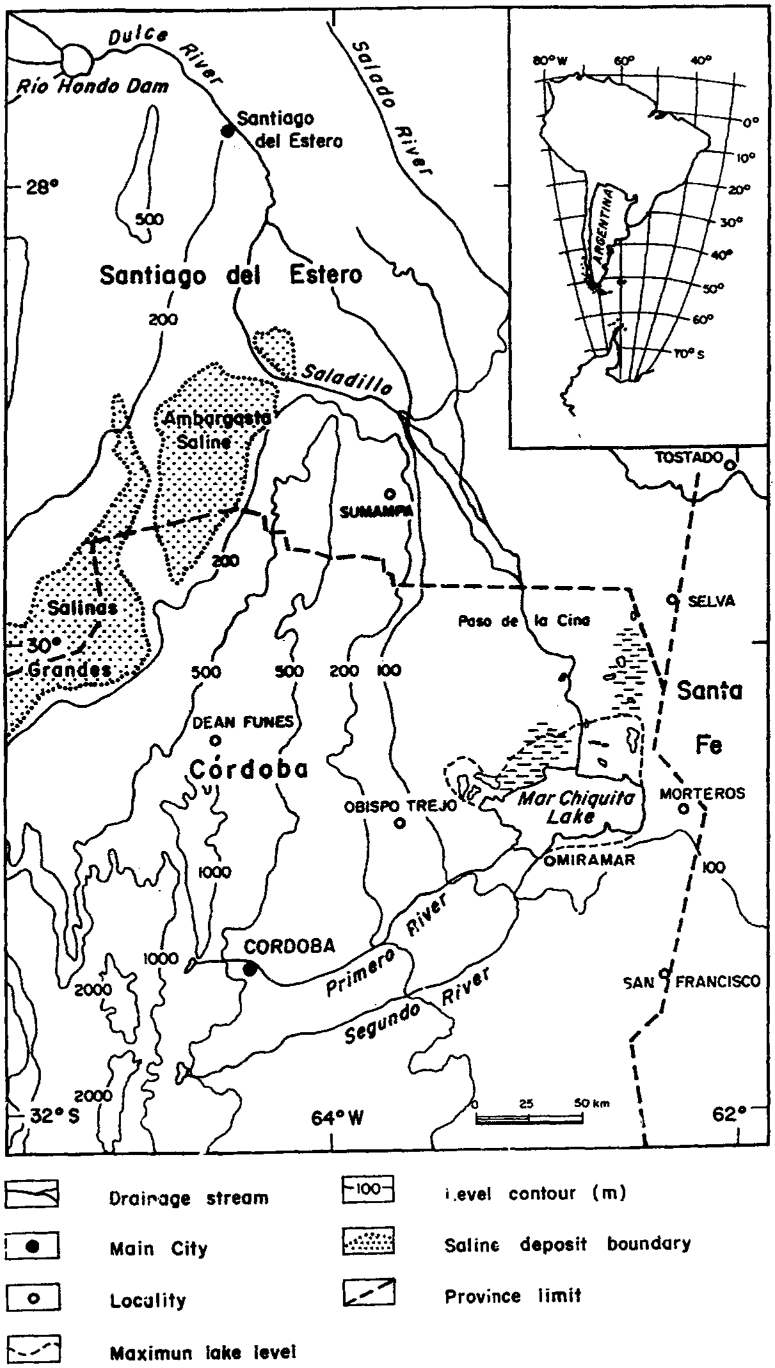

Fig. 1. Location map.

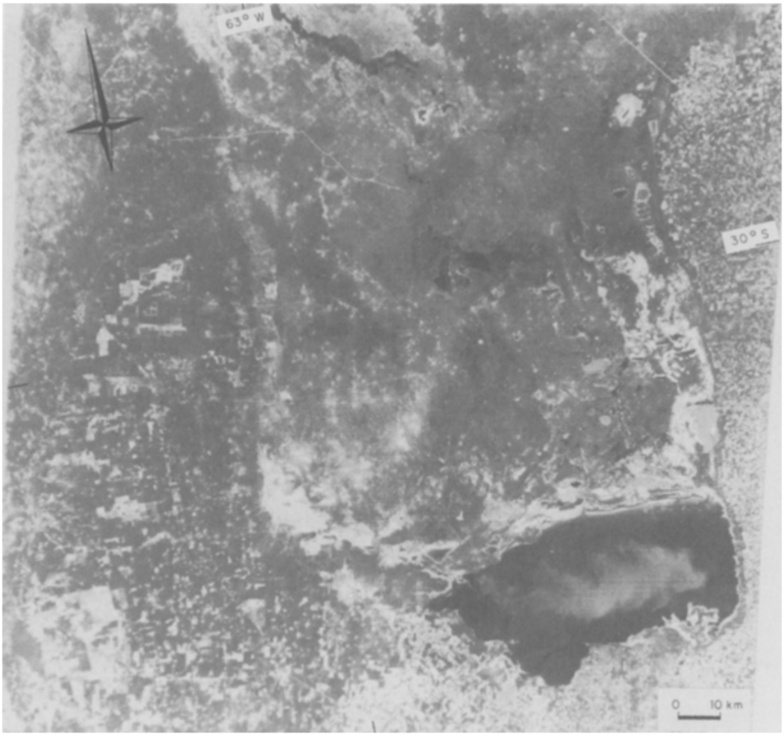

Fig. 2. Landsat image of December (lake area: 1,800 km^2).

the lake the main economic activity is cattle production, with some farming also.

The ecological value of the area is very high: a relict of the 'bosque chaqueño oriental' plant community develops on its shores, and there is a wide diversity of native fauna, its avifauna in particular remarkable for having 294 species (30 per cent of the total species in the country). Since 1966, the Government of the Province of Córdoba has designated the area as a Natural Reservation.

The ecosystem of the lake and human activities are closely related to physico-chemical conditions in the lake. These vary greatly according to long-term climatic cycles. Thus, during historical times the lake has been at lower levels, with an area of about 2,000 km^2 (Fig. 2), a depth of 4 m, and with hypersaline waters. Salinities of 225 g/L in 1912 (Frank, 1912), 180 in 1935 (Kanter, 1935), 290 in 1953 (Bertoldi, 1953), and 282 in 1970 (D.P.H., 1970) have been reported. Since 1973, a significant increase in mean rainfall has led to an increase in the volume of the lake, with a rise in water-level of

Fig. 3. Landsat image of August 1981 (lake area: 5,000 km^2).

4 m and an increase in surface area to 5,000 km^2 (Fig. 3). As a result, salinity decreased to 78.7 g/L in 1977 (Durigneux, 1978), 29.9 in 1982 (C.A.De.N.E., 1982), 28.7 in 1986 (Martínez, 1991) and 35.4 in 1989 (Martínez, 1991) (Fig. 4). These changes have had a significant impact on the ecosystem and human activities. The tourist facilities and agricultural areas were flooded and the muddy shores became steep shorelines. Furthermore, several fish species appeared, notably the 'pejerrey' (Osteichtyes: Atherinidae), an atherinid fish of special economic interest. Moreover, estimates of salt mass must be updated according to the changes in salinity and ionic composition.

On the basis of the application of a chemical equilibrium model, this paper analyses the effect of the changes in concentration on the ionic composition of the lake. It does so in order to contribute to a better understanding of changes in the environment.

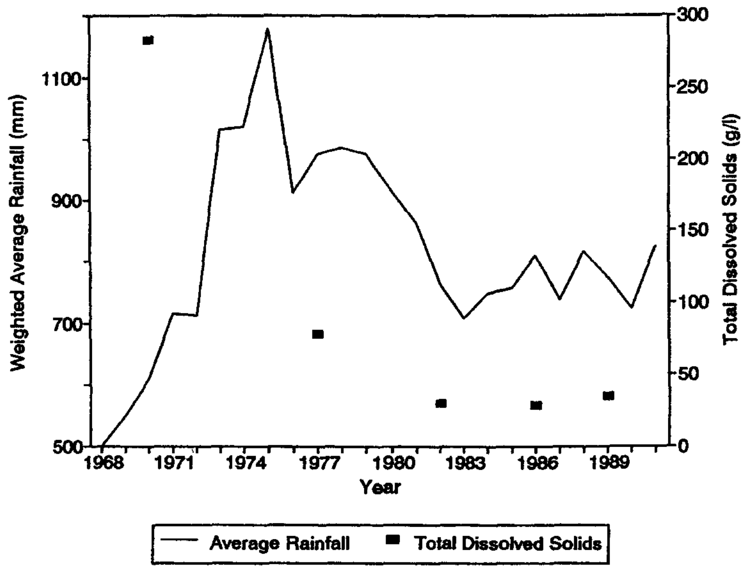

Fig. 4. Weighted average rainfall and total dissolved solids evolution.

Methods

The analytical data have been obtained from several sources. The most recent determinations (1986, 1989) correspond to collections made by the author. For their collection and analysis the sampling and analytical methods followed by the United States Geological Survey (Brown *et al.*, 1970) were used.

Previous information is scarce. A representative analysis of the composition of the lake's water before its level increased (1970), one at concentrations after the increase of rainfall (1977), and three analyses of its composition in recent times (1982, 1986, 1989) when the lake was least saline, have been used for the geochemical modelling (Table 1).

The first thermodynamic calculations were carried out using the program WATEQ4F (Plummer *et al.*, 1976). This program uses for the activity coefficient calculation an extended form of the DebyeHückel equation (Truesdell and Jones, 1974), which includes a final term (+bI). It has been used to compute activity coeffients in solutions having ionic strengths as high as 4.0. Nevertheless, the study of Harvie and Weare (1980) showed that at NaCl molar concentrations higher than 1.0, the extended Debye-Hückel model solubility predictions for gypsum solubility exhibit an error which ranges between 25 and 50 per cent, while Pitzer's equations were found to model accurately mineral solubilities. Then, the program PHRQPITZ (Plummer *et al.*, 1988) was used for the geochemical calculations. This program incor-

Table 1. Mean concentrations and standard deviations (in parenthesis) of major ions and other parameters for different dates.

	Year 1970	Year 1977	Year 1982	Year 1986	Year 1989
Number of Samples	8	16	8	57	91
Temperature °C	–	–	–	22.9	27.8
pH	–	8.00 (0.20)	8.53	8.30 (0.10)	8.53 (0.13)
Density	–	1.056	1.019	–	1.022
Dissolved Oxygen (mg/l)	–	–	–	9.45 (1.95)	4.73 (1.83)
Total dissolved solids (mg/l)	282,756	78,690 (1,901)	29,916	28,079 (942)	35,242 (1,980)
Calcium (mg/l)	1,021	521.9 (17.6)	261.0	284.3 (10.2)	349.7 (18.5)
Magnesium (mg/l)	720.0	357.7 (6.63)	146.0	171.6 (5.4)	246.1 (15.7)
Sodium (mg/l)	107,730	27,690 (833)	10,703	9,964.5 (327.2)	12,522 (719.9)
Potassium (mg/l)	1,558	279.9 (7.88)	164.0	131.2 (2.53)	141.0 (8.21)
Chloride (mg/l)	143,691	36,490 (791)	13,620	13,411 (464.3)	16,654 (973.5)
Sulphate (mg/l)	27,910	11,800 (289)	4,460	4,208 (155)	5,098 (311.5)
Bicarbonate (mg/l)	0.0	148.6 (9.82)	481.0	293.2 (21.2)	208.0 (16.24)
Carbonate (mg/l)	126.3	0.0	11.6	0.0	26.4 (5.44)
Sulphide (mg/l)	–	–	–	–	0.01
Fluoride (mg/l)	–	–	–	0.352 (0.02)	0.412 (0.03)
Lithium (mg/l)	–	9.7 (0.2)	0.3	0.36 (0.01)	0.476 (0.01)
Silica (mg/l)	–	–	–	–	4.35 (1.38)

porates Pitzer's equations to program PHREEQE (Parkhurst *et al.*, 1980). PHRQPITZ has been applied to the modelling of the hypothetical processes that led from the mean tributary composition to the different compositions of the lake in time.

Characteristics of the area

Hydrology and climate

Mar Chiquita Lake is the terminus of an extensive, closed basin into which the Primero River (the 'Suquía' in the Comechingones indigenous language) and Segundo River (Xanaes) to the south, and the Dulce River to the north converge. The latter is the most important river in the basin, with a mean discharge of 141.4 m^3/s in the hydrological cycle of 1980–1987. The mean discharge of the Primero River was 10 m^3/s and of the Segundo River 14.3 m^3/s in the hydrological cycle of 1961–1980. The present climatic conditions in the area range from semi-arid to semi-humid. The rainfall (1930–1970) fluctuated between 700 and 800 mm/year. About 80 per cent of the rainfall occurs in summer. A rainfall gradient which decreases from east to west is present and decreases from an average of 825 mm/year in Morteros to 560 mm/year in Deán Funes. The vapour tension decreases in the same direction, resulting in a uniform hydraulic balance throughout the area, with a water deficit of about 100 mm/year. The mean temperature between November 20 and March 25 is 24.5 °C, while for the rest of the year mean temperature is 11.5 °C.

Origin and recent geological evolution

Mar Chiquita Lake occurs in the geological basin referred to as 'Llanura Chaco-Pampeana' (Russo *et al.*, 1979). This basin is a pericratonic basin in which the basement, formed by Precambrian and Early Palaeozoic igneous and metamorphic rocks, has been found at variable depths between 1,000 and 3,500 m below the land surface, and is affected by a tectonic fault network. Overlying the basement, there is a sequence of sedimentary and volcanoclastic rocks of Palaeozoic, Upper Mesozoic and Cenozoic age. The origin of the surface-hydrologically closed basin is the post-Pliocene elevation of the Selva-Tostado horst (Stappenbeck, 1926), a rectangular block enlarged over 400 km in the N–S direction, in the line of Tostado-Morteros-San Francisco (Fig. 1), forming a ridge of about 30 m on the western side. The elevation of this structure has blocked the outflow of rivers to the east towards an open basin (the Paraná River basin), thus forming the closed system.

The lake, initially a freshwater body, had its origin in the Upper Pleistocene (Castellanos, 1956) during a humid period referred to as 'Lujanense' (Ameghino, 1889) between 10,000 and 30,000 years B.P. (Martínez, 1991). Arid and semi-arid climatic cycles have alternated between the Lujanense period and the present (Cantú and Degiovanni, 1984). Upper Pliocene-Holocene sediments constitute the geological environment of the lake. They are especially loess-like silt or sandy-silt sediments of eolian and fluvio-eolian origin, with sandy intercalations. The source area of the sediments is mainly located in the Sierras Pampeanas ridge, to the west of the basin, and is formed of Precambriam and Lower Palaeozoic granitic and metamorphic (mainly gneiss) rocks.

Origin of the salinity

The high concentration of total dissolved solids results from the progressive accumulation of salt because of the deficit hydraulic balance of the basin. The dissolved salts are carried mainly by the inflowing streams, especially the Dulce River. This river has a dry branch running across a saline deposit, the Salar de Ambargasta, and during sporadic floods this develops a high salinity, so imparting a high saline load to the Dulce River. Because of this phenomenon, Frank (1912) referred to the Mar Chiquita as a 'migrated saline'. During one of these episodes on November 1 1988, Martinez (1989) recorded a salinity in the Dulce River of 22.846 g/L at Paso de la Cina, which returned to its normal concentration of about 1.00 g/L just four days later (November 5, 1988).

The weighted average ionic composition of the discharge of the tributaries has been calculated on the basis of hydrochemical sampling of the major rivers and other streams (Martínez, 1991), but the result may be different from the real mean composition as a consequence of the difficulty of evaluating the incidence of these rare high salinity episodes in the Dulce River. The calculated mean composition in equivalents per cent is: a) cationic: Na^+ 67.56, K^+ 2.13, Mg^{2+} 9.44, Ca^{2+} 20.85; b) anionic: CO_3^{2-} 0.08, HCO_3^- 18.07, SO_4^{2-} 28.71, and Cl^- 53.14.

Results

The average composition of available data, expressed in equivalent percentages (Table 2), has been plotted in a Piper diagram (Fig. 5). The variations resulting from the changes in salinity are small, but show a clear trend. The dominant cation is sodium, but there is a continuous increase of calcium concentration from 1970 to 1989. Chloride is the dominant anion, and it decreases

Table 2. Mean composition in meq per cent for different dates and average tributary composition.

Year	1970	1977	1982	1986	1989	A.T.C.
Calcium	1.05	2.09	2.68	3.12	3.02	20.85
Magnesium	1.23	0.73	0.77	0.96	1.10	9.44
Sodium	96.90	96.60	95.69	95.18	95.24	67.56
Potassium	0.82	0.57	0.86	0.74	0.63	2.13
Chloride	87.38	80.37	79.16	80.37	80.97	53.14
Sulphate	12.53	19.18	19.13	18.61	18.29	28.71
Bicarbonate	0.00	0.19	1.62	1.02	0.59	18.07
Carbonate	0.09	0.26	0.08	0.00	0.15	0.00

A.T.C.: Weighted average tributary composition

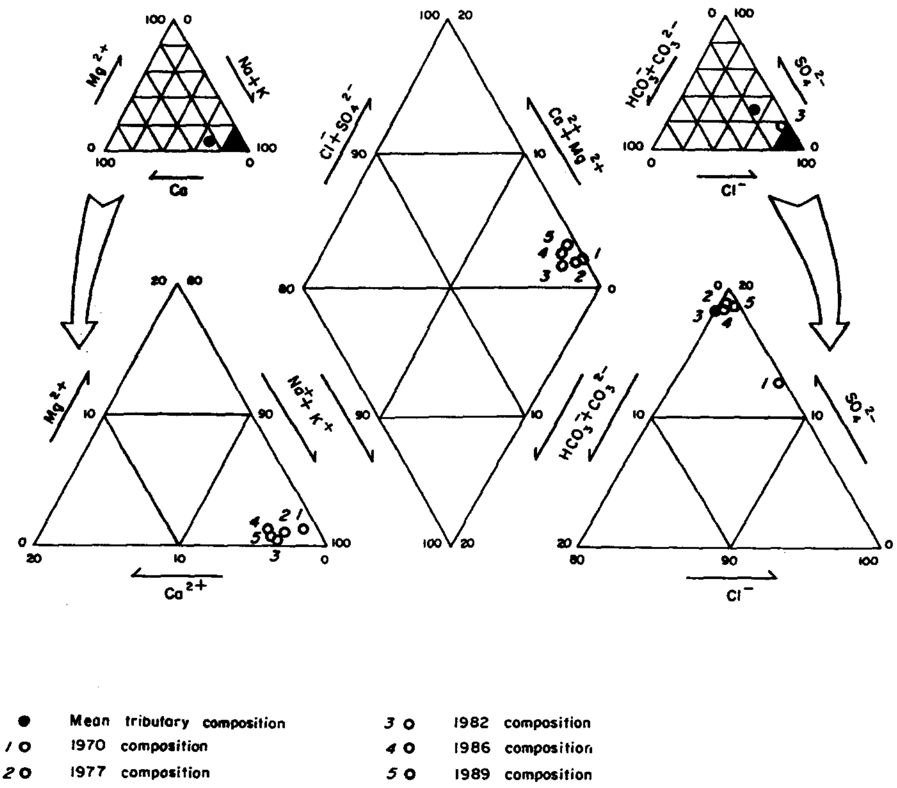

Fig. 5. Piper diagram of the observed Mar Chiquita and mean tributary composition.

about 7 meq per cent from 1970 to 1989, with sulphate increasing in a similar percentage. Moreover, an increase in the bicarbonate concentration was recorded from 0.19 meq per cent in 1970 to 1.62 meq in 1989.

The mean ionic composition of Mar Chiquita is widely different from the composition of mean surface input. The differences are due to chemical processes which take place in solution. Martínez (1991), on the basis of observations on data from two sets of samples collected from all parts of the surface and water column in 1986 and 1989, each set of which included 57 and 93 samples respectively, noted that:

(i) The composition of the water is very homogeneous throughout the lake. This is shown in the very small standard deviations and variation coefficients, lower than 6 per cent in all cases.

(ii) The statistical distribution of the ions analysed adjusts itself to the normal law, that is, the statistical model of the chemical equilibrium according to Smirnov (1963).

(iii) There are highly significant correlations between the concentrations of all the major ions.

According to observed differences between the discharge weighted average composition of the tributaries and the mean composition of the lake, the existing processes lead to a proportional decrease in calcium, magnesium and sulphate concentrations, and result in a water that is typically dominated by sodium and chloride. The most reasonable proposal is that the main process regulating the composition of Mar Chiquita is the chemical equilibrium with solid phases such as calcite and gypsum. Studies on the sand fraction mineralogy of 31 bottom sediment samples (Martínez *et al.*, in press) have clearly differentiated two groups (Table 3). The first corresponds to the centre of the lake, where gypsum crystals are the main mineral (sometimes more than 80 per cent), with minor proportions of quartz, shell fragments and feldspar. The second one corresponds to the marginal samples, where volcanic glass, quartz, muscovite and feldspars are the dominant minerals, with gypsum, tourmaline, biotite, priroxenes and opaque minerals only accessory. The clay fraction mineralogy has been analyzed for 14 samples (Table 3). Illite is the main clay mineral, with subordinate smectites interstratified in variable proportions and with little kaolinite. Calcite is very abundant in most samples, especially the central ones.

To explore these concepts further, a geochemical model of the different solutions was carried out which calculated the activity coefficients (Table 4) and the saturation indices with respect to these minerals (Table 5). An evaporative process, taking the mean tributary composition as the initial solution, has been modelled using the program PHRQPITZ (Plummer *et al.*, 1988). The progressive concentration has been simulated adding hypothetical reactions

Table 3. Sand fraction mineralogy and X-ray clay mineralogy (from Martínez *et al.*, in press).

I. Sand fraction mineralogy (31 samples)

	Main minerals	Accessories
A. Central samples	gypsum, shell fragments, quartz	volcanic glass, feldspar, muscovite
B. Marginal samples	quartz, volcanic glass, muscovite, feldspar	tourmaline, piroxenes, biotite, opaque minerals

II. Clay fraction X-ray mineralogy (clay minerals in percentages)

Sample	Smectite plus Interstratified	Illite	Kaolinite	Quartz	Feldspar	Calcite
SM2	28	70	2	Scarce	Scarce	Abundant
SM3	17	80	3	Abundant	Scarce	Scarce
SM6	38	61	1	Abundant	Scarce	Abundant
SM7	15	84	1	Abundant	Scarce	Scarce
SM8	7	90	3	Abundant	Scarce	Scarce
SM10	20	77	3	Abundant	Scarce	Scarce
SM12	26	70	4	Abundant	Scarce	Abundant
SM13	32	66	2	Abundant	Scarce	Abundant
SM14	23	73	4	Abundant	Scarce	Abundant
SM17	27	70	3	Abundant	Scarce	Abundant
SM20	15	81	4	Abundant	Scarce	Abundant
SM22	22	75	3	Abundant	Scarce	Abundant
SM29	16	80	4	Abundant	Scarce	Abundant
SM31	32	63	5	Abundant	Scarce	Scarce

at different steps, according to the chloride ratios between the mean tributary composition and different lake compositions. The observed equilibrium features have been included, noting the degree of calcite saturation and the pCO_2, and the equilibrium with gypsum. Finally, reactions representing the removal of cations by aluminosilicate clay synthesis have been added. The relationship between the observed and the simulated compositions at different steps for 1986 and 1977 is discussed below.

Discussion

The rainfall increase since 1973 led to a significant increase in the volume of the lake, with a corresponding decrease in ionic strength: from 6.648 in

Table 4. Activity coefficients for major ions (from PHRQPITZ).

Year	1970	1978	1982	1986	1989
Sodium	1.582	0.679	0.687	0.691	0.685
Potassium	0.766	0.588	0.646	0.651	0.637
Magnesium	3.989	0.236	0.215	0.226	0.226
Calcium	2.126	0.197	0.197	0.206	0.195
Bicarbonate	0.207	0.467	0.574	0.582	0.558
Carbonate	0.003	0.041	0.091	0.090	0.074
Sulphate	0.006	0.052	0.120	0.126	0.105
Chloride	0.631	0.582	0.641	0.644	0.629

Table 5. Effective ionic strength and saturations indices for different dates.

Year	1970	1977	1982	1986	1989
E.I.S	6.689	1.509	0.555	0.531	0.663
Anhydrite	0.651	−0.369	−0.774	−0.745	−0.625
Aragonite	1.525	0.560	1.142	0.741	0.922
Brucite	−1.749	−3.181	−2.948	−3.452	−2.546
Calcite	1.711	0.747	1.330	0.929	1.107
Dolomite	4.033	1.596	2.934	2.142	2.625
Epsomite	−2.340	−2.844	−3.296	−3.194	−3.100
Gypsum	0.624	−0.186	−0.568	−0.527	−0.445
Halite	−0.045	−1.828	−2.664	−2.695	−2.520

E.I.S.: Effective ionic strength

1970 to a minimum of 0.541 in 1986. These changes produced a modification in the saturation conditions for the major ions in relation to different minerals (Fig. 6). Before 1973, the solution was oversaturated with sulphate and carbonate species, and near to saturation for NaCl, as a consequence of the high solute concentration. Carbonate, sulphate and calcium concentrations were low. With the rise in the lake level and the decrease of the ionic strength, the thermochemical conditions in the solution were modified in a significant way. At the salinity prevailing in 1977 (77.8 g/L), gypsum equilibrium was reached. Following subsequent dilution, the ionic strenth continued decreasing (1982, 1986) and the solution became undersaturated in gypsum and anhydrite producing an increase in the sulphate concentration from 12 meq per cent to 18 meq per cent, and in the calcium concentration from 2

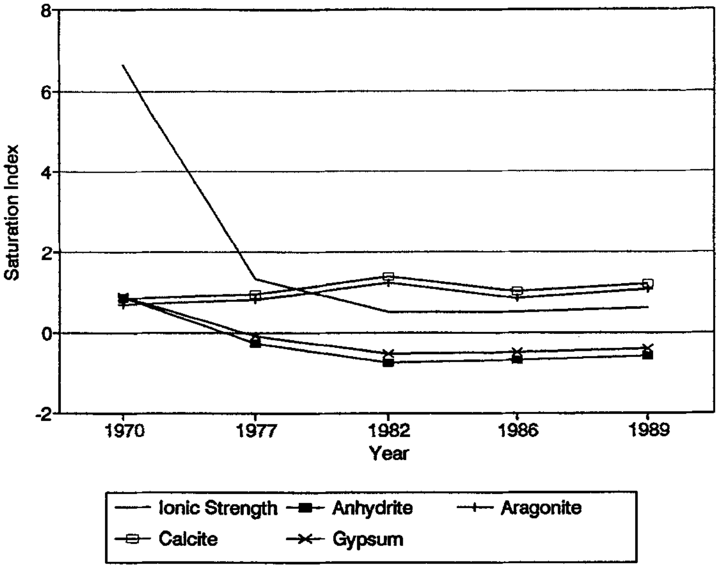

Fig. 6. Evolution of ionic strength and saturation indices.

meq per cent to 3 meq per cent. Simultaneously, an increase in the calcite and dolomite saturation indices took place due to the common ion effect. The presence of finely crystalline calcite in the clay fraction and gypsum crystals in the sand fraction of the bottom sediments (Martínez *et al.*, in press) supports the equilibrium model hypothesis. Gypsum is not present in the X-ray diagrams of the clay fraction, probably since crystallization results only in sand/silt sized crystals. A fresh increase in ionic strength in 1989 produced only little change with respect to features of the 1986 solution. The inclusion of silica in the model for 1989 modifies the program output, including the saturation indices of silicate minerals and adding the common ion effect in some cases. The saturation indices of calcite and gypsum changed very little. The modelled solution is undersaturated with respect to the silica group of minerals (amorphous silica, quartz, cristobalite) and fluorite, and oversaturated in the magnesium silicate minerals chrysotile and sepiolite. These last minerals were not recognized in the bottom sediments.

The simulation of an evaporative process using PHRQPITZ shows different degrees of adjustment to the observed compositions according to the reactions considered. The differences between a pure evaporative process and the observed composition are noticeable. At this stage, with the obvious exception of chloride, most of the ions are in excess in the modelled composition. Including the equilibrium conditions with calcite, gypsum and pCO_2 according to the thermodynamic model output, bicarbonate, calcium and sodium concentrations approximate the observed composition. Nevertheless, an important excess of sulphate, magnesium and potassium concentrations remain.

At this point, some other field and laboratory observations made on Mar Chiquita Lake should be highligted. First, the bottom sediments of the lake constitute an anoxic environment, as indicated by its smell and especially by the mean sulphide concentration of 10.48 mg/L in interstitial waters (Martínez, 1991). Second, an important proportion of the bottom sediments consists of argillaceous minerals, especially illite.

Thus, two different mechanisms can be proposed to explain the observed composition. On the one hand, there is good evidence that in the bottom environment the reducing conditions lead to sulphate reduction and sulphide formation, which of course give rise to the characteristic smell and provide a source for the uptake of sulphate. Moreover, a significant decrease between surface and the bottom sulphate concentrations has been found by applying analysis of variance to the samples collected at different depths in 1986. The reaction that can explain the sulphate uptake is:

$$3SO_4 + C_6H_{12}O_6 \Longrightarrow 3H_2S + 6HCO_3^- \qquad (1)$$

This involves a release of bicarbonate from organic matter to the solution. This reaction is produced by *Desulfovibrio* bacteria, which have been identified in the lake by Seckt (1945) and Debillerbeck (1979). On the other hand, it is important to account for the synthesis of typical clay minerals from degraded aluminosilicates, in reactions of the type:

$$\begin{aligned}&\text{X ray amorphous Al silicate} + SiO_2 + \text{cations} \Longrightarrow\\&\text{cation Al silicate} + CO_2 + H_2O\end{aligned} \qquad (2)$$

The importance of these reactions in the marine environment has been highlighted by Sillen (1961) and Mackenzie and Garrels (1966). They have been extrapolated to Mar Chiquita on the basis of the similar saline features and the illite and smectite concentrations in the bottom sediments as determined by Martínez *et al.* (in press) (Table 5). The removal of some quantities of sodium, magnesium and potasium by reaction with degraded aluminosilicates to form sodic montmorillonite or illite appears a reasonable process, according to the reactions:

$$\begin{aligned}&3.5Al_2Si_{2.4}O_{5.8}(OH)_4 + Na^+ + 2.6SiO_2 + HCO_3^- \Longleftrightarrow\\&3Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + CO_2 + 4.5H_2O\end{aligned} \qquad (3)$$

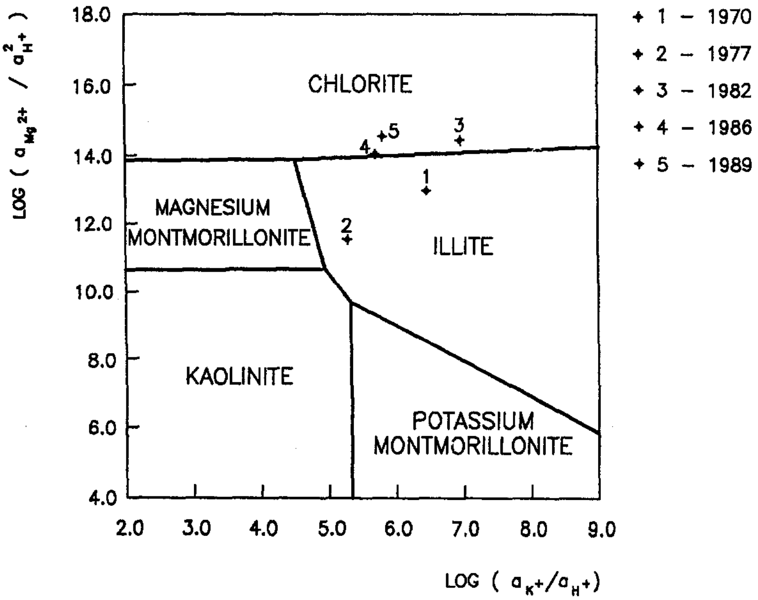

Fig. 7. Stability diagram of clay minerals. $a_{H_2SiO_4} = 10^{-3.87}$

$$Al_2Si_{2.4}O_{5.8}(OH)_4 + 5Mg^{2+} + 0.6SiO_2 + 10HCO_3^- \Longleftrightarrow Mg_5Al_2Si_3O_{10}(OH)_8 + CO_2 + 3H_2O \quad (4)$$

$$2.5Al_2Si_{2.4}O_{5.8}(OH)_4 + K^+ + SiO_2 + HCO_3^- \Longleftrightarrow K_{0.5}Al_{2.5}Si_{3.5}O_{10}(OH)_2 + CO_2 + 3.5H_2O \quad (5)$$

As indicated, illite is dominant in the clay fraction of the bottom sediments. A significant amount of the illite is probably detrital in origin, but existing interstratified minerals could represent intermediate clay minerals/siliceous phases in the neoformation process. The stablity diagram (Fig. 7) shows the equilibrium of the solution with illite. These reactions have been included in the modelling of the water composition using PHRQPITZ. The model has been applied to the mean tributary composition in an attempt to obtain ionic compositions similar to those observed in 1977 and 1986.

The evaporative processes have been simulated by adding to the initial solution (mean tributary composition) the appropiate ion proportions to obtain the observed chloride concentration. The resulting solution was equilibrated with calcite, gypsum and PCO_2 at the saturation values given by PHRQPITZ. Finally, a reaction with the molar proportions according to Equations (1) to (5) has been included to obtain a simulated composition which approximates to the real composition. These molar proportions are: 0.05 mol from reaction

Table 6. Geochemical modelling of the solution evolution from mean tributary composition to observed 1977 composition (using PHRQPITZ) (1) evaporation simulation to the observed chloride content; (2) fixing the calcite, gypsum and pCO_2 observed equilibrium conditions; (3) adding clay formation and sulphate reduction reactions. All values in mmol/L.

	Modeled composition			Measured composition
	(1)	(2)	(3)	
pH	7.18	8.31	8.24	8.00
Ca^{2+}	195.63	9.59	11.69	13.02
Mg^{2+}	92.63	92.63	15.63	14.71
$Na^+ + K^+$	1311.39	1311.39	1285.32	1211.68
Cl^-	1029.38	1029.98	1029.98	1029.98
SO_4^{2-}	277.93	259.30	153.51	122.84
$HCO_3^- + CO_3^{2-}$	350.00	4.20	3.17	5.77

Table 7. Geochemical modelling of the solution evolution from mean tributary composition to observed 1986 composition (using PHRQPITZ) (1) evaporative simulation to the observed chloride content; (2) fixing the calcite, gypsum and pCO_2 observed equilibrium conditions; (3) adding clay formation and sulphate reduction reactions. All values in mmol/L.

	Modeled composition			Measured composition
	(1)	(2)	(3)	
pH	7.28	8.41	8.29	8.30
Ca^{2+}	71.98	4.65	6.70	7.09
Mg^{2+}	34.06	34.06	6.16	7.06
$Na^+ + K^+$	495.87	495.87	446.17	436.82
Cl^-	378.33	378.33	378.33	378.33
SO_4^{2-}	102.21	93.22	44.12	43.80
$HCO_3^- + CO_3^{2-}$	128.72	7.53	5.18	4.81

(1), 0.03 mol from reaction (3), 0.027 mol from reaction (4) and 0.01 mol from reaction (5) for each 0.48 increase in the ionic strength. It is possible to accept these rates for the modelling of other different solution concentrations.

The results of the modelling, shown in Tables 6 and 7 and in Schoeller's diagrams in Figs. 8 and 9, are in good agreement with measured concentrations, including pH values. The adjustment of the HCO_3^--modelled concen-

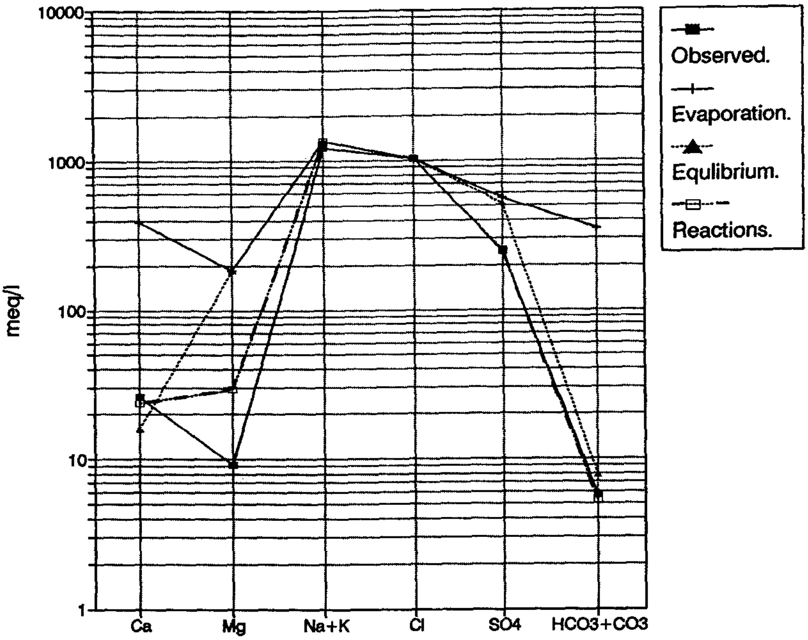

Fig. 8. Schöeller diagram of the modelled 1977 composition.

tration to the observed value support the selected reactions. Bicarbonate is present in the four reactions as a reactant or a product. Also noticeable is the fact that the sum of the moles of bicarbonate added or sustracted gives a bicarbonate concentration near to real concentration. The proposed sequence is close to a modified Hardie-Eugster model (Hardie and Eugster, 1970). The result attained also accords with the Hardie-Eugster model. For solutions with an alkalinity < 2 [Ca^{2+}] after calcite precipitation, this model predicts a gypsum precipitation which leads to a chloride-sulphate brine if [SO_4^{2-}] > [Ca^{2+}]. This is the case for Mar Chiquita. The model modifications include clay formation and the redox process. Field observations and bottom sediment mineralogy support the introduction of these processes.

Conclusions

Analysis of the evolution of salinity and consideration of the physical and chemical features of the environment leads to an hypothesis on the origin of the ionic composition of the waters of Mar Chiquita. This hypothesis suggests that the composition of its waters had its origin in the concentration by evaporation of the mean tributary composition. The composition of the concentrated solution was modified by equilibrium and redox chemical processes.

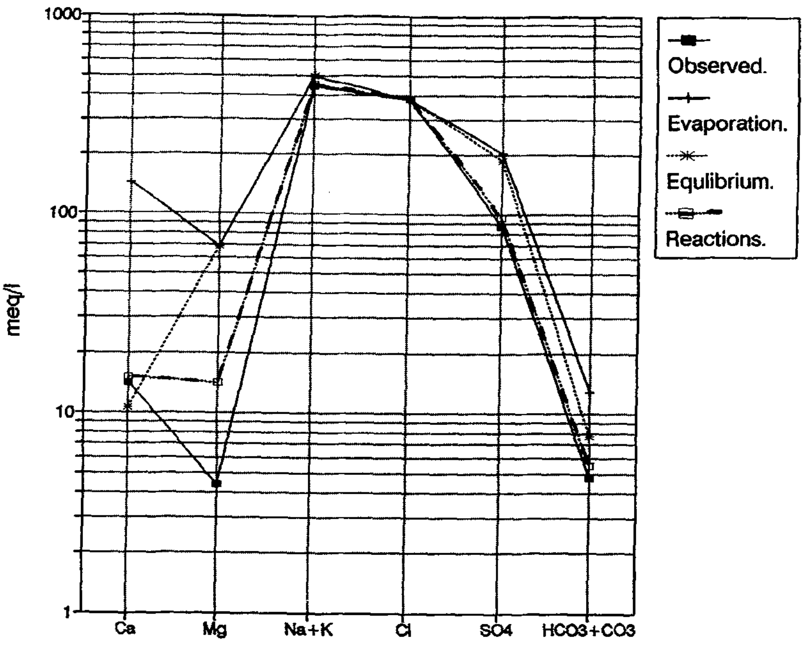

Fig. 9. Schöeller diagram of the modelled 1986 composition.

Applying a hydrogeochemical model based on field observations, it has been possible to establish those processes which regulate the composition of the water at different concentrations. Five particular conclusions can be noted. First, the ionic composition of the waters of Mar Chiquita is the consequence of chemical equilibrium conditions with regard to mineral phases existing in bottom sediments. The most important processes are calcite and gypsum equilibrium, sulphate reduction and neoformation of clay minerals. Second, the thermochemical state of the solution was strongly modified following the increase in the rainfall after 1973, leading to a decrease in the effective ionic strength from 6.61 in 1970 to 0.501 in 1986. Third, the solution moved from supersaturation in calcite and gypsum conditions to conditions of gypsum undersaturation because of dilution. Gypsum undersaturation led to an increase in sulphate and calcium concentrations and to the rise in the calcite saturation index due to the common ion effect. Fourth, at the 1970 salinity (280 g/L), which is near the dominant salinity during this century, the solution was close to NaCl saturation. At the 1977 salinity (78 g/L), the solution was close to gypsum equilibrium. Finally, the evolution of the composition of the solution from the composition of that in the initial mean tributary agrees with the Hardie-Eugster model.

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